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CORRELATION AND COLLECTIVE MODES IN NARROW BAND MATERIALS: NiO --ETCIU

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cont.

superconductivity of the dynamical response of electrons and especially coupling via plasmons or excitons is being studied for Cu<sub>2</sub>O. It is shown that there may be a connection between experiments on copper oxides which show nearly complete shielding of electric fields and experiments which show excitons in the oxide may obey Bose-Einstein statistics. More careful calculations for this and other transition metal oxides are discussed.

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CORRELATION AND COLLECTIVE MODES IN NARROW  
BAND MATERIALS: NiO AND FeO

1. Introduction

The background for most of the work described in this report has been given previously and no attempt is made to repeat it here. The reader who wants further details should refer to the original or continuation proposals entitled "Correlation and Collective Modes in Narrow Band Materials: NiO and FeO," under Grant No. AFOSR-80-0023. The progress in this research during the past year is described in Section III. An important new component of our studies of electronic excitations and collective modes is work on the effect of plasmons and excitons on superconductivity in transition metal oxides which is described in Section III-C.

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### II. Research Objectives

The overall objective of this research is to study the effects of electronic excitations, especially plasmons and interband excitations, on the properties of materials for which these effects are significant. The materials we have chosen are narrow band systems, such as the transition metal oxides. For these materials, it is necessary to emphasize their localized properties and, especially, strong electron-lattice interactions in constructing the correlation and response functions. In the first year of this work, we have set up this description of the electronic structure in terms of a local orbitals approach and have begun some calculations.

Our studies of electronic correlation and its effect on the band structure have begun with TiO. We will continue with investigations of systems where the effects of electronic excitations are even stronger, such as FeO and NiO. For these systems interband excitations become quite prominent and complicate the optical or electron energy loss spectra. We will also continue our studies of collective modes for these systems, such as plasmons, in the presence of strong lattice interactions.

We are investigating the contributions of electronic excitations to quantities which can be measured experimentally. Presently we are analyzing the electronic loss structure of TiO and FeO. In the future we will extend this analysis to NiO and other narrow band systems. We will want to know how the loss structures due to plasmon and interband excitations behave in these materials, and we will want to develop methods for explaining the significant changes that occur in some cases when the surface is contaminated or the material is implanted with impurities. From these studies we hope to develop an important tool for explaining the effects of surface or bulk contamination on these systems.

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A. D. BLOSE  
Technical Information Officer

We are investigating plasmon and exciton coupling in the establishment of superconductivity for narrow band systems. We will want to know how electrons coupled by these mechanisms shield external fields, and what effect the strong coupling has on the superconducting properties. We have begun studies on Cu<sub>2</sub>O for which some interesting experimental evidence exists. In the future we will move to other transition metal oxides.

### III. Progress

#### A. Correlation in Narrow Band Materials.

The effect of correlation on the band structure of a material is contained in the self-energy matrix  $\sum_{\vec{k}}$ . To find the correlated energy bands and wave functions, one solves the energy dependent matrix equation

$$\left[ \underline{H}_0 + \sum_{\vec{k}}(\omega) \right] \vec{A}(\omega) = E(\omega) \vec{A}(\omega) \quad (3.1)$$

where  $\underline{H}_0$  is, for example, a one-electron Hamiltonian such as Hartree Fock (HF) and  $\omega$  is the frequency. Now in general we must diagonalize Eq. (1) to find the energy bands  $E(\omega)$ . However, if the diagonal terms in  $\underline{H}_0 + \sum_{\vec{k}}$  are dominant, the correlated energy bands are just

$$E_{\vec{k}} = E_{\vec{k}}^{\text{HF}} + \sum_{\vec{k}}^D(\vec{k}, E_{\vec{k}}) , \quad (3.2)$$

assuming that  $\underline{H}_0$  is the HF Hamiltonian. The self-energy to second order in the coulomb interaction between Bloch states is

$$\begin{aligned} \sum_{n_1 n_2}^2 (\vec{k}, \omega) &= \sum_{\substack{m' m \\ \ell, \vec{k}', \vec{q}}} V_{n_1 \vec{k} m} V_{m' \vec{k}+q, \ell \vec{k}'+\vec{q} \vec{m} \vec{k}'} \\ &\times \frac{V_{m \vec{k}' \ell \vec{k}'+\vec{q}, m' \vec{k}+\vec{q} n_2 \vec{k}}}{\omega + E_{\ell \vec{k}'+\vec{q}} - E_{m \vec{k}'} - E_{m' \vec{k}+\vec{q}}} \\ &+ \sum_{\substack{\ell' m \\ \ell, k, q}} (m' \rightarrow \ell') \frac{1}{\omega + E_{m \vec{k}'} - E_{\ell \vec{k}'+\vec{q}} - E_{\ell' \vec{k}+\vec{q}}} \end{aligned} \quad (3.3)$$

where  $(m' \rightarrow \ell')$  signifies that the second set of  $V$ 's is the same as the first except that  $m'$  is replaced by  $\ell'$ . Here  $V$  refers to the coulomb interaction,

and  $m$  always refers to particle Bloch states ( $E_m > E_F$ ) while  $\ell$  always refers to hole states ( $E_\ell \leq E_F$ ).

There is a great savings in computational effort to be had by converting Eq. (3.3) into a sum over Wannier states (for details see proposal for continuation of AFOSR-80-0023). This savings makes the solutions of Eqs. (3.1-3.2) possible. The transformation of Eq. (3.3) to the Wannier representation requires use of the relation

$$a_n(\vec{r}-\vec{R}_1) = \frac{1}{\sqrt{N}} \sum_{BZ} \psi_{nk}(\vec{r}) e^{i\vec{k}\cdot\vec{R}_1} \quad (3.4)$$

between the Wannier and Bloch states where  $N$  is the number of unit cells and  $n$  is the band index. Thus we must remove factors like  $e^{i\vec{k}\cdot\vec{R}_1}$  from the coulomb matrix elements in Eq. (3.3) so that we have the sum

$$\frac{1}{N} \sum_{k'q} \frac{e^{-i(\vec{k}'+\vec{q})\cdot(\vec{R}_1-\vec{R}_1')} e^{iq\cdot(\vec{R}_2-\vec{R}_2')}}{\omega + E_{\ell\vec{k}'+\vec{q}} - E_{m\vec{k}'} + E_{m'\vec{k}+\vec{q}}} \quad (3.4')$$

Then the  $V$ 's are matrix elements over the Wannier states. We see that the sums over band index in Eq. (3.3) are limited to states above or below the Fermi level, and this restriction will reduce computational effort. More importantly our Wannier functions are restricted to the band, complex which contributes most strongly to correlation in a given energy region of the band structure. We will see that this group of bands can be much smaller than the total number of bands.

The effect of correlation on the valence bands of NiO and FeO is still not fully explained. Especially for NiO, the detailed structure and width of the d-band region is uncertain. We are planning on doing calculations of correlation corrections for these two materials, but first we have undertaken a calculation of  $\langle \rangle^2$  in Eq. (3.3) for TiO. This material was the subject of some controversy a few years ago. An ab-initio Hartree Fock calculation by Jennison and Kunz<sup>1</sup>

showed hybridized oxygen 2p and titanium 3d bands with no energy gap between them. These results differed sharply from local exchange calculations<sup>2</sup> which show a band gap of at least 2eV between the oxygen 2p and titanium 3d bands. Experimental X-ray photoemission results [by Ichikawa et al.<sup>3</sup>] for what was evidently TiO seemed to support the Jennison and Kunz calculation. However, later experiments<sup>4</sup> showed that the Ichikawa samples must have oxidized to become TiO<sub>2</sub> and thus the d band structure in the XPS spectrum was missing.

The correct TiO spectra<sup>4</sup> had a band gap and were in agreement with the local density calculations. Subsequently, Kunz<sup>5</sup> argued that the gap was due to correlation corrections neglected in the Hartree Fock calculation and asserted that relaxation would raise the d bands with respect to the p bands. Our calculation should test Kunz' assertion and will also provide an assessment of correlation effects.

We have included 9 bands in the TiO self-energy calculation which arise from the titanium 4s and 3d states and the oxygen 2p states. The other bands are well out of the valence - conduction band region, and we consider them to not contribute much to the self-energy near the Fermi surface. Except for a small region around the  $\Gamma$  point in the uncorrelated band structure where all the bands are above the Fermi level, three bands are occupied, three are unoccupied, and three are partly occupied. Thus by working in the Wannier representation, we have an immediate partitioning and need only consider 6 bands for the occupied states and 6 bands for the unoccupied states.

The self-energy calculation still requires a major computational effort in spite of the partitioning. We must evaluate the self-energy matrix at k-points throughout the Brillouin zone and at frequencies  $\omega$  which cover the valence band energies for each k-point. In the TiO calculation we have chosen 10 frequency points at each k to evaluate  $\sum_{\omega}^{\infty}(k, \omega)$  and must interpolate between the solutions of Eq. (3.1) to find  $E_n = E(E_n)$  for a given band n. We have used every possible

symmetry to make the calculation manageable. The computation of the Wannier coefficients

$$c_{n\alpha}(\vec{R}_1) = \sum_{\vec{k}} c_{n\alpha}^{\vec{k}} e^{i\vec{k}\cdot\vec{R}_1} \quad (3.5)$$

is greatly reduced by the fact that all rotations of the lattice set are equivalent and thus we need calculate only one  $c_{n\alpha}(\vec{R}_1)$  for each shell of atoms. Furthermore, since our system has inversion symmetry, we can choose  $c_{n\alpha}^{-k} = c_{n\alpha}^{k*}$  and thus Eq. (3.5) becomes

$$c_{n\alpha}(\vec{R}_1) = \sum_{\vec{k}} \operatorname{Re} \left\{ c_{n\alpha}^{\vec{k}} e^{i\vec{k}\cdot\vec{R}_1} \right\} \quad (3.6)$$

The index  $\alpha$  normally runs over all the basis functions in the basis set (e.g., 40 functions for TiO). This number of functions can be reduced to 9, the number of bands in our complex, by variationally choosing optimized basis functions.<sup>1</sup> However, since in this case we are using local orbitals which are in a sense already optimized for each band, we may simply choose the 9 local orbitals contributing most to the Bloch functions in our band complex. Once calculated, the  $c_{n\alpha}(\vec{R}_1)$  is used to construct the coulomb matrix elements  $V_{n_1 R_1, n_2 R_2; n_3 R_3, n_4 R_4}$  which appear with expression (3.4') in the construction of  $\sum_{\vec{k}, \omega}^2$ . If we suppress the band indices  $n$  and basis functions indices  $\alpha$ , we may write the coulomb matrix element as

$$\begin{aligned} V_{\vec{R}'_1, \vec{R}'_2; \vec{R}'_3, 0} &= \sum_{\vec{R}_1 \vec{R}_2 \vec{R}_3 \vec{R}_4} C(\vec{R}_1 - \vec{R}'_1) C(\vec{R}_2 - \vec{R}'_2) C(\vec{R}_3 - \vec{R}'_3) \\ &\times C(\vec{R}'_4 - \vec{R}_4) V_{\vec{R}_1 - \vec{R}_4, \vec{R}_2 - \vec{R}_4; \vec{R}_3 - \vec{R}_4, 0} \end{aligned} \quad (3.7)$$

showing that we need only consider interactions which include the origin in our sum. Since the sum in Eq. (3.3) involves only certain combinations of occupied and unoccupied bands, not all matrix elements  $V'$  need be evaluated.

The final term appearing in  $\sum^2$  is the expression appearing in (3.4'). This expression is similar in structure to the free electron polarization and thus we call it  $\chi(\vec{k}; \vec{R}_1, \vec{R}_2)$ . We may write (3.4') as

$$\chi(\vec{k}; \vec{R}_1, \vec{R}_2) = \sum_{\vec{k}, \vec{q}'} \chi(\vec{k}, \vec{k}', \vec{q}'; \vec{R}_1, \vec{R}_2) \quad (3.8)$$

again suppressing all band indices. To calculate every element in Eq. (3.8) would require a large amount of time and a massive amount of storage. Fortunately, not every element need be calculated since many are related by symmetry. The basic relation is

$$\chi(R\vec{k}, R\vec{k}', R\vec{q}; \vec{R}_1, \vec{R}_2) = \chi(\vec{k}, \vec{k}', \vec{q}; R^{-1}\vec{R}_1, R^{-1}\vec{R}_2) \quad (3.9)$$

where  $R$  is a rotation belonging to the rotation group of the crystal. In particular Eq. (3.9) indicates that we need calculate  $\chi$  for only those  $\vec{k}$  values in an irreducible wedge of the Brillouin zone if we include all rotations of the other variables. Furthermore all rotation of the type  $R'\vec{k} = \vec{R}\vec{k}$  where  $R\vec{k}$  has already been calculated need not be redone.

We have written computer codes to handle the above three elements which go into the  $\sum^2$  calculation. These codes employ all the symmetry relations we have discussed. The calculation of the matrix elements  $V$  in Eq. (3.7) requires a major effort. We have used very efficient quantum-chemistry computer codes for calculating two-electron integrals over Gaussians.<sup>6</sup> By fitting each local orbital to contracted sets of Gaussians, we are able to write the matrix elements  $V$  in terms of the Gaussian integrals.

The transformation in Eq. (3.7) is then carried out using quantum chemistry integral transformation programs for configuration interaction calculations.

We use only up to next nearest neighbors in the sum over  $\vec{R}_1, \vec{R}_2$  in Eq. (3.3) for our TiO calculation since we find adding more shells of atoms do not affect the major results of the correlation calculation. We have only gotten results for TiO at  $\vec{k}=0$  so far, but these indicate that the  $\Gamma_{12}^{(d)}$   $_{15}^{(p)}$  points move away from one another as Kunz expected. We will need to calculate other points in the zone, however, before we can make out the positions of the correlated bands. Our results indicate that the diagonal elements of  $\sum_L^2(\vec{k}, \omega)$  give a qualitative picture of the correlation effects even without diagonalizing Eq. (3.1).

After we complete the TiO studies, we will use the procedures we have developed to study correlation in NiO and FeO. For these studies we will need self-consistent energy bands and wave functions in a Gaussian basis. We have implemented bands structure codes here due to Wang and Calloway<sup>7</sup> and have modified them to accept two atoms per unit cell for these calculations.

#### B. Electron Energy Loss Structure of Clean and Oxidized Transition Metals.

The characteristic energy loss structure of a material provides a direct measure of the contributions from interband transitions and collective modes such as plasmons to the electronic excitation spectrum. The loss structure is altered by changes in bulk properties and also by surface modification or adsorption, particularly certain features which are quite sensitive to adsorption. In addition, since the loss structure provides a direct measure of plasmon energies and intensities, one can use it to test the basic understanding of these modes. These tests are especially important for systems with strong crystal potentials, such as the transition metals, where the plasmon behavior is not expected to follow the simple free-electron result.

Unfortunately there is qualitative disagreement between the experimental results themselves, and in addition the results have been given different interpretations so that very different energies for plasmons and interband transitions have been reported. To clean up the confusion, we have undertaken a careful reexamination of the loss structure for certain transition metals<sup>8</sup> by analyzing a new series of measurements made by Keith Legg in our department. These measurements are for clean and oxidized polycrystalline iron samples and also clean and oxidized polycrystalline titanium samples for comparison. This analysis fits into the objectives of this program since it has allowed us to clearly identify plasmon structures and has provided data for comparison with the more basic theoretical calculations we have undertaken.

The characteristic loss structure measurements fall into two classes: measurements of losses suffered by electrons with energies of many kilovolts as they are transmitted through thin films and measurements of losses suffered by electrons with energies around 100eV as they are reflected from the material. The former experiments are dominated by electrons which do not undergo elastic scattering while the latter are more highly resolved but contain electrons which have been elastically scattered at least once. The two types of spectra for evidently clean Ti surfaces are shown in Fig. 1<sup>9,10</sup>. There are large qualitative differences between the spectra at energy losses below 20eV, especially between the lower reflection spectrum and the transmission spectrum. The data from our measurement for clean Ti, which is a reflection measurement, is shown in Fig. 2a. It is more highly resolved than the reflection data in Fig. 1a, but it is qualitatively in agreement with it.

Our analysis of the clean Ti data is as follows. The peak around 5eV is undoubtedly a surface peak since it is quite sensitive to surface contamination and since it is less pronounced for higher primary electron energies as shown in Fig. 1a. The latter behavior is consistent with a surface excitation since

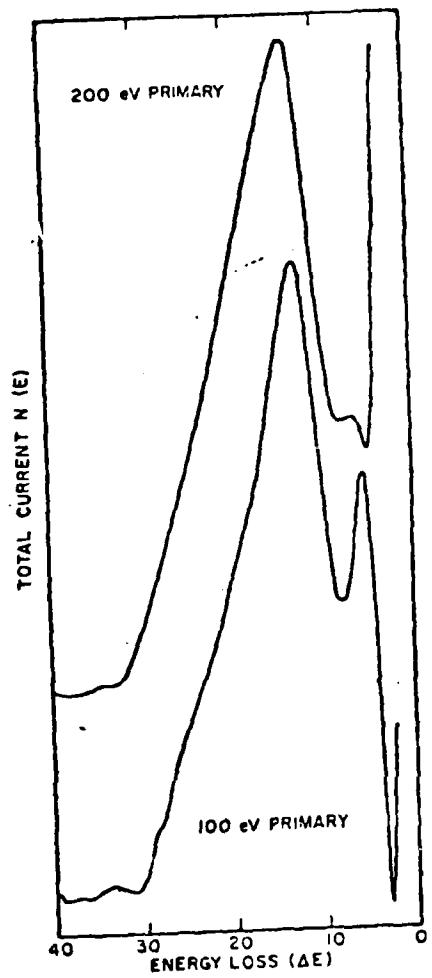


Fig. 1a Energy loss spectrum  
of clean titanium.

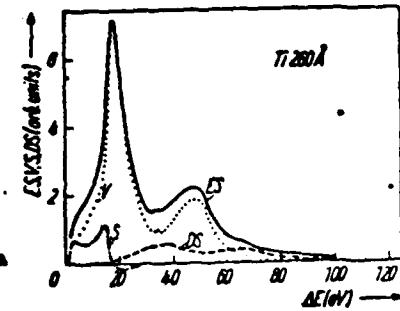


Fig. 1b Transmission energy  
loss spectrum (full  
curve) for a titanium  
film.

the mean free paths of the primary electrons are greater at higher energies which means the bulk signal would be enhanced with respect to the surface. We have identified this peak tentatively as a surface plasmon in agreement with Simmons and Scheibner<sup>9</sup> (SS) since collective modes should be more prominent at this energy relative to interband excitations. However we need to confirm this identification with further measurements and analysis of how the intensity of this peak changes as the scattered electrons deviate from the specular direction. An intensity maximum at an angle away from the specular direction would indicate that the peak is a surface plasmon.<sup>11</sup> The prominent peak at about 10eV is the volume plasmon. The structure extending below this peak for about 20eV probably contains the second volume and surface-volume contributions postulated by SS, though our higher resolution data shows this structure to be less prominent than theirs. However, we also find a double peaks at about 35eV which also appears in the appropriate place in the iron data, and we identify this as the split ( $\frac{1}{2}, \frac{3}{2}$ ) Ti 3p interband excitation.

The loss spectrum changes greatly upon adsorption of only a monolayer of oxygen. Most significantly, the surface peak disappears completely and new losses appear around 20eV and 45eV. The sensitivity of the spectrum to oxygen points out one of the causes for differences between the measurements of others workers. Only carefully cleaned Ti specimens in a vacuum of  $10^{-8}$  Torr or less exhibited the true clean surface loss spectrum. We identify enhancement in loss structure at about 20eV as due to the O 2s interband excitation. A similar structure appears in the same place in oxidized iron. The peak at about 45eV is more mysterious. Transmission measurements for Ti (presumably partly oxidized)<sup>10</sup> and TiO<sup>12</sup> show this structure quite prominently in both the loss spectrum and the imaginary part of the dielectric function  $\epsilon_2$  derived from a Kramers-Kronig analysis. Its appearance in  $\epsilon_2$  means it is not a collective mode

and must be an interband transition. A similar peak does not appear in the oxidized iron spectrum (see Fig. 3b), and there are no interband losses expected in this region. No strong explanation has ever been offered for this peak, though it could be a double interband excitation or an excitation to a higher conduction band. It seems possible that the structure is connected to the metal 3p peak since it appears about 9eV above this peak for both titanium and vanadium.<sup>13</sup> It could be a double excitation involving the metal 3p and O 2p electrons, but it would be surprising that such a process would be stronger than the 3p excitation alone. We certainly need further theoretical analysis here and have undertaken an investigation of the calculated loss spectrum in this region.

But what about the differences between the transmission spectrum for Ti in Fig. 1b and our reflection spectra in Fig. 2? Fig. 1b most resembles Fig. 2b because the transmission sample undoubtedly had an oxide layer. However this does not explain the difference in energy between the volume plasmon peaks in the two experiments, and this difference is important in an analysis of collective modes in transition metals since the transmission spectrum places the plasmon near its free electron value while the reflection spectrum does not. Fig. 1a and also reflection experiments on vanadium done at several primary electron energies<sup>13</sup> indicate that the plasmon peak moves to higher energy as the primary energy increases. These results imply that the differences between the plasmon peaks in the two spectra may be due to the great difference in primary energies used. A primary energy increase would lessen the lateral spread of the electron beam due to multiple scattering for a given target thickness. However, in the reflection experiment as the primary energy increases, the depth of the target probed increases also. We can do a crude calculation based on the plural scattering theory which should give us an estimate of the lateral spread for electrons transmitted through a 300 Å film at 35 keV and for reflected

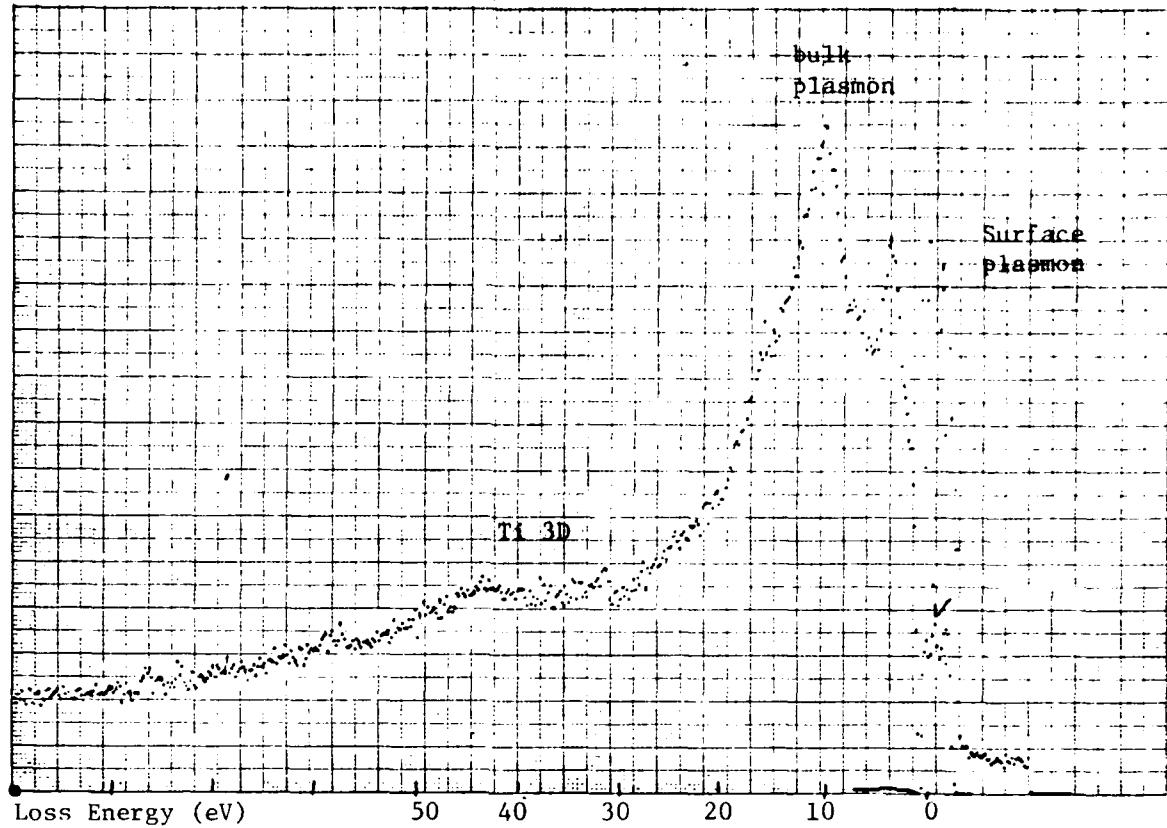


Fig. 2a Loss spectrum for clean titanium 200 eV primary.

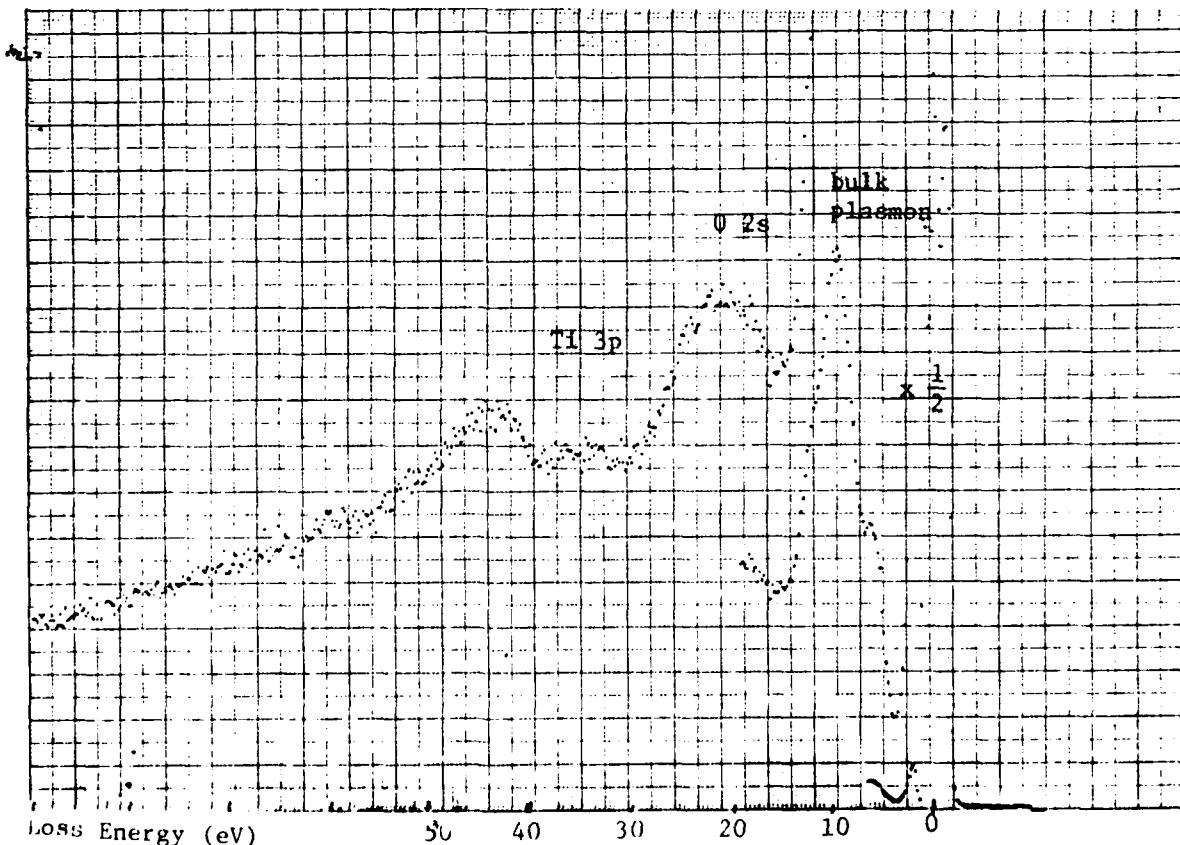


Fig. 2b Loss spectrum for Titanium + Oxygen

electrons at 100eV which go through about 20 Å. The calculation shows that the transmitted electrons have a spread in momentum transfer of several times  $k_f$ . Thus even though the spectrum in Fig. 1b had an analyzer acceptance angle for scattered electrons of only about 5 mrad.<sup>10</sup> which corresponds to a momentum transfer of less than .3  $k_f$  for Ti, there must be a great deal of scattering of electrons with larger momentum transfers back into this region. The dispersion of the plasmon is

$$\omega_l(q) = \omega_p + \alpha(\hbar/m)q^2 \quad (3.10)$$

in an RPA-like theory. Since  $\alpha$  is positive, dispersion increases the plasmon energy and would result in the effect noted for the transmission experiment as well as significant peak broadening. For Al the dispersion is as much as 13eV,<sup>14</sup> so it is possible to have an average peak shift of several eV. We thus conclude that the peak shift in the transmission experiment is due to dispersion and that, in this case, the reflection experiment peak is closer to the true volume plasmon energy.

Our loss spectra for clean and oxidized polycrystalline iron, shown in Fig. 3, have some similarities with the titanium spectra. The volume plasmon peak at 15eV is well below the free electron value of about 30eV, and the spin-orbit split Fe(3p) transition is clearly visible in the appropriate place at about 55eV. However, in contrast to titanium, the interband excitations are much stronger in the iron spectra. The region below 10eV is dominated by interband excitations from the iron d-bands which completely cover the effect of the surface plasmon. As the oxide grows a pronounced O 2s peak appears at about 19eV and grows larger than the volume plasmon. The structure below 10eV is also changed due to the growth of the O 2p peak and some charge transfer from the surface d bands. The peak at about 45-50eV does not appear in the

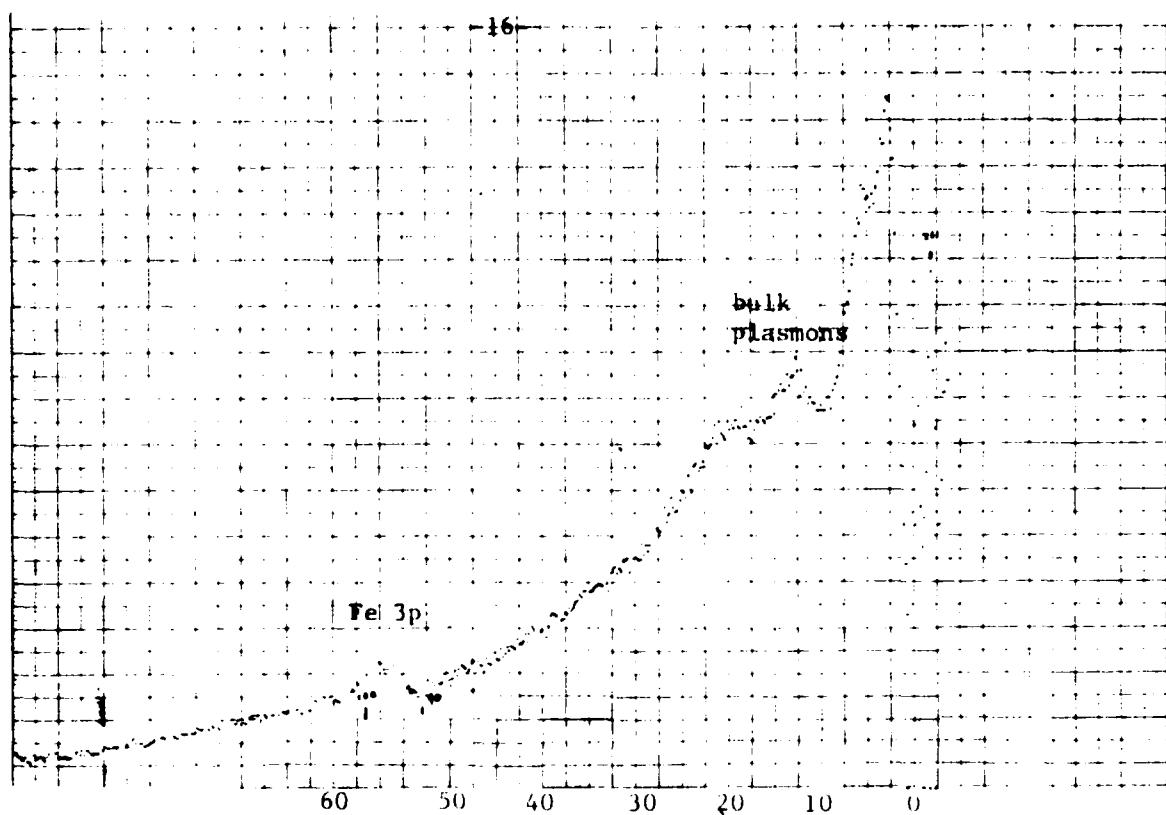


Fig. 3a Loss spectrum for clean iron 200 eV primary energy.

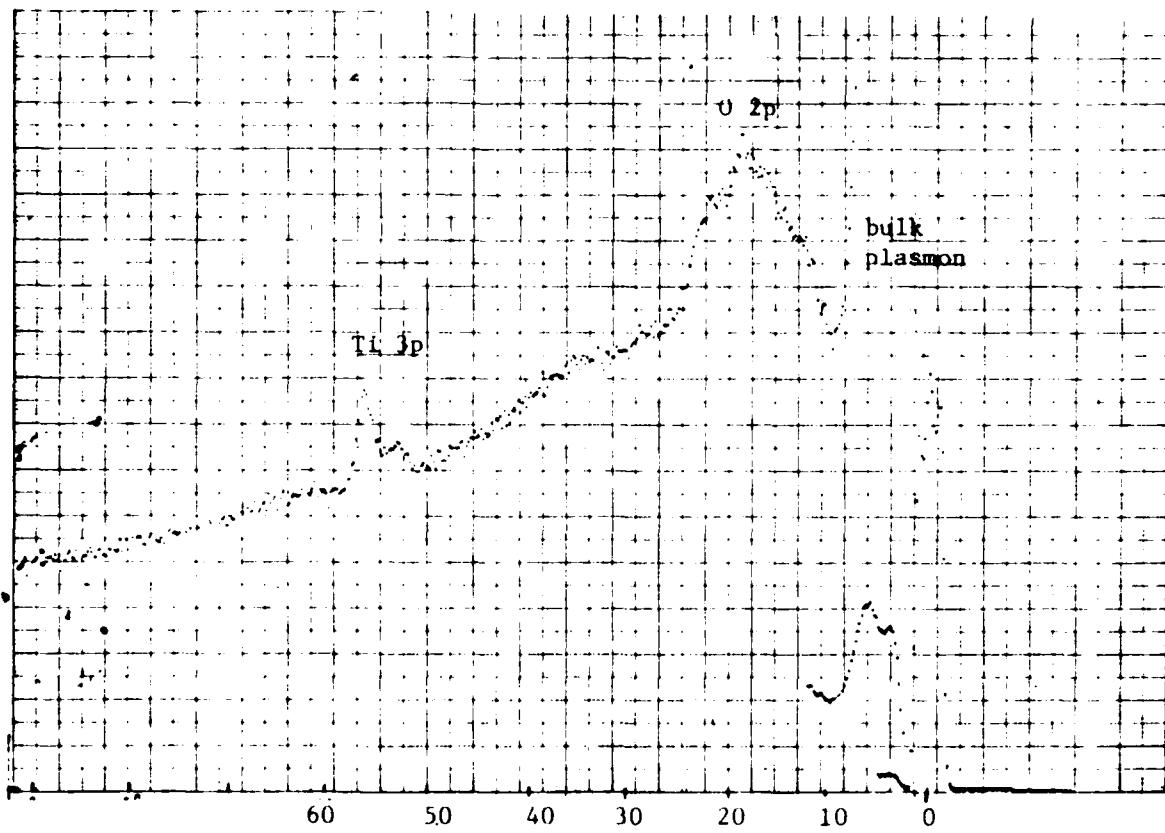


Fig. 3b Loss spectrum for iron + oxygen.

oxidized loss spectrum as it does for Ti and V which is consistent with the idea that it is connected with the metal 3p band. However, it does not appear beyond the Fe 3p peak either in Fig. 3b. The inelastic electron transmission loss data for iron<sup>10</sup> differs from the reflection data in a similar manner to that from titanium. Here again we believe the multiple scattering caused as the electrons traverse the sample mixes in plasmons from a large range of momentum transfers and results in a shift of the plasmon peak to higher energy. We are presently calculating the band structures for both iron and iron oxide with the intent of making a comparative study of how band structure and transition probabilities affect the loss processes.

C. Effects of the Dynamically Screened Coulomb Interaction on Bose Condensation and Superconductivity.

We have recently extended our investigation of the dynamical response of electron in transition metals to the conditions of Bose condensation and superconductivity. The usual BCS theory of superconductivity<sup>15</sup> approximates the term involving the coulomb interaction as a constant, but the inclusion of the dynamical interaction allows the study of a rich variety of effects caused by plasmons and excitons. Up to recently ideas about the existence of strong effects of this type were merely speculative, but some experimental evidence now suggests that the effects may exist for some systems.<sup>16,17</sup> Also, calculations indicate that these effects should be enhanced in two dimensional systems such as surfaces or interfaces.<sup>18,19</sup> All this work improves the prospects of finding condensates with unusual properties or high critical temperatures.

We have been exploring ways to add more accurately the band structure effects to the calculations of the properties of these Bose Einstein systems. Local field effects are assumed to significantly affect the critical temperatures of certain excitonic systems, although there is disagreement about whether the

temperature is enhanced<sup>20</sup> or depressed.<sup>21</sup> These arguments are based on a qualitative analysis and a more quantitative analysis for specific two-dimensional and three-dimensional systems, such as we have undertaken, would be quite useful.

We are exploring the properties of systems with the Hamiltonian,

$$H = \sum_{n,k} E_n^k c_{n\sigma}^{\dagger} c_{n\sigma}^k + \frac{1}{2} \sum_{p,k} \sum_q V_{n_p n_q}^0 c_{p\sigma}^{\dagger} c_{q\tau}^{\dagger} c_{k-q\tau} c_{p+q\sigma} \quad (3.10)$$

where  $p=n_p, p+q=n_q, q, \dots$  and we have suppressed the indices of the Coulomb matrix element  $V_{n_p n_q}^0 \dots$ . The index  $n$  refers to band  $n$ ,  $E_n^k$  is a band energy, and all matrix elements are over Bloch states. The anomalous Green's function in the Gor'kov ladder approximation would then be at  $T=T_c^{18}$

$$F_n(p, i\omega_p) = \frac{1}{(i\omega_p)^2 - \epsilon_p^2} T \sum_{\Omega_q} \sum_q V_{nn}(q, i\omega_q) \\ \times F_n(p+q, i\omega_p + i\omega_q). \quad (3.11)$$

where  $\omega_p = \pi T(2p+1)$  and  $\omega_q = 2\pi T q$ , with  $p$  and  $q$  integers. The quantity  $V_{nn}(q, i\omega_q)$  is the effective interactions between electrons in the  $n$ 'th band, and we have assumed that intraband interactions dominate interband interactions. The effective interaction may be written

$$V_{nn}(q; i\omega_q) = (V_0^{-1}(q, i\omega_q))_{nn} \quad (3.12)$$

where the parentheses  $(\dots)_{nn}$  indicates the diagonal matrix element of the product of  $V_0$  and  $\epsilon_{nn}^{-1}$ . If we were to neglect local field effects, then

$$\epsilon_{nn}^{-1}(q, i\omega_q) \rightarrow \frac{1}{\epsilon_{nn}(q, i\omega_q)}$$

and we could use the usual dielectric function in the analysis of Eq. (3.11). This analysis has been done for the case of weak - coupling superconductors with a very simple plasmon pole approximation for general surface and bulk systems<sup>18</sup> and a more complicated screening function for a Si(111)-SiO<sub>2</sub> interface system.<sup>19</sup> We plan to study the influence of local field effects on the critical temperature in the weak-coupling case for some transition metal oxides. Since the plasmon or exciton mediated coupling may not be small at all, we will also look at the strong-coupling case for these systems using the theory of Eliashberg.<sup>22</sup>

Measurements by Witteborn and Fairbank<sup>16</sup> have established the existence of an anomalously weak electric field outside the surface of copper at low temperatures. Analyses have shown that one should expect a combined electric field due to gravitationally induced strain fields and patch fields of the order  $10^{-6}$  V/m,<sup>23</sup> but, in fact, the electric field is only about  $10^{-11}$  V/M below 4.5°K. Above 4.5°K a phase transition seems to occur,<sup>16</sup> and the electric field outside the copper surface is in the expected range. Many analyses which suggest mechanical or electronic explanations of this phenomenon have been put forth, but perhaps the most likely and most intriguing explanation is that the surface electrons couple and obey Bose-Einstein statistics at low temperatures.<sup>23</sup> They then form a Bose condensate below 4.5°K. The coupling mechanism would be something other than phonons, perhaps excitons or plasmons. The possibility of superconductivity below the transition temperature is also being explored. Since the copper surface in the experiments is covered with an oxide of some 20 %,<sup>16</sup> this shielding effect must take place in or near the oxide. Now very recent experiments on Cu<sub>2</sub>O<sup>17</sup> indicate that an exciton gas formed in this material by laser excitation obeys Bose-Einstein statistics. This may be the mechanism we need to explain the

anomalous shielding effect seen by Witteborn and Fairbank since their copper oxide was most likely reduced and could have been  $\text{Cu}_2\text{O}$ .

Madey and Hanni have made an estimate of the density of surface bosons needed to provide the observed shielding of the ambient electric field above 4.5°K. Their result is about  $10^{11}$  bosons/cm<sup>2</sup> which is in the low density region where exciton or plasmon coupled superconductivity is expected to be enhanced.<sup>18,19</sup>

However, if, for example, one assumes the excitons in  $\text{Cu}_2\text{O}$  behave like an ideal Bose gas, the volume condensation temperature is<sup>17</sup>

$$T_{c_\infty} = \frac{m_0}{m} \left( \frac{n}{g6.2 \times 10^{15}} \right)^{2/3} \quad (3.13)$$

where  $m_0$  is the free-electron mass,  $m$  is the particle mass,  $g$  is the degeneracy factor, and  $n$  is in units of cm<sup>-3</sup>. For  $\text{Cu}_2\text{O}$ ,  $m/m_0 \sim 3$  and, since the most likely exciton state to obey Bose-Einstein statistics is the triplet,<sup>17</sup>  $g=3$ . Assuming a volume density of  $n=(10^{11})^{3/2}$ , the result from Eq. (3.13) is

$T_{c_\infty} = .329^\circ\text{K}$ . However, we are dealing with an essentially two-dimensional system for which Ginzburg and Kirshnits<sup>24</sup> estimate the transition temperature for an ideal Bose gas should be

$$T_c = \left( dn^{1/3} / \ln(Adn) \right) T_{c_\infty} \quad (3.14)$$

where  $d$  is the film thickness and  $A$  is the film area. With  $d=20 \text{ \AA}$  and  $A \sim 100 \text{ cm}^2$ ,  $T_c = 2.32 \times 10^{-3} T_{c_\infty} = .76 \times 10^{-3}^\circ\text{K}$ . This temperature is considerably below the observed transition temperature. As Ginzburg and Kirshnits observe,<sup>24</sup> Eq. (3.14) may underestimate the transition temperature since superconducting films of thickness  $d \sim 30 \text{ \AA}$  and  $T_c \approx T_{c_\infty}$  exist.

Unfortunately the ideal gas result, Eq. (3.13), is probably an upper limit to  $T_c$ . For finite exciton coupling constant  $\lambda$  the critical temperature would be lower and still well below the transition temperature observed. This discrepancy is a serious defect in explanations of the anomalously weak electric field in terms of screening by a Bose condensate.

A review of the screening calculations of Madey and Hanni<sup>23</sup> indicates that assuming an ideal Bose gas composed of coupled free electrons may overestimate the screening. The electric field in the surface region due to the system of substrate and surface electrons and ions is<sup>23</sup>

$$\epsilon = -\frac{1}{e} \frac{\partial \mu}{\partial z} - \frac{ma}{e} \quad (3.14)$$

where  $\mu$  is the chemical potential of the electrons and  $a$  is the acceleration due to gravity. Now since  $\mu$  varies mainly through the change in the surface density  $n_s$ ,

$$\begin{aligned} \frac{\partial \mu}{\partial z} &= \frac{\partial \mu}{\partial n_s} \frac{\partial n_s}{\partial z} \\ &\approx \frac{1}{4\pi e^2 d} \frac{\partial \mu}{\partial n_s} \epsilon_z. \end{aligned} \quad (3.15)$$

The last expression involves an estimate of the variation of  $n_s$  due to the substrate electric field  $\epsilon_z$  which involves both patch fields and gravitationally-induced lattice compression fields. The quantity  $\frac{1}{4\pi e^2 d} (\frac{\partial \mu}{\partial n_s})$  is then the shielding factor. Now, for an uncondensed ideal Bose gas in two-dimensions,  $\mu$  is defined by the expression

$$n_s = \frac{2}{2\pi} \int d^2 k \left\{ e^{\beta(E_o + \frac{1}{2}k^2 / 2m_o - \mu)} - 1 \right\}^{-1} \quad (3.16)$$

where  $\beta = 1/k_B T$  and  $E_o$  is the ground state energy. The integral in Eq. (3.16)

is analytic in the two-dimensional case and the result is

$$\mu = \beta^{-1} \ln \left[ 1 - \exp(-2\pi\hbar^2 n_s \beta / m_o) \right] + E_0 \quad (3.17)$$

the electric field at the surface state is then

$$-\frac{1}{e} \frac{\partial \mu}{\partial z} \approx \frac{\hbar^2 \epsilon_z}{2e^2 dm} \left[ \exp \left( \frac{2\pi\hbar^2 n_s \beta}{m_o} \right) - 1 \right]^{-1} - \frac{m_o a}{e}. \quad (3.18)$$

It is Eq. (3.18) that Maday and Hanni use to fit the experimental data of Witteborn and Fairbank with an  $\epsilon_z \sim 10^{-6}$  V/m and  $n_s \sim 10^{11}$  cm<sup>-2</sup>.

We can include the band structure effects on the excitonic gas in Cu<sub>2</sub>O as before, with an effective mass replacing the electron mass in Eq. (3.16). The degeneracy factor g should also multiply the integral in Eq. (3.16), and the result for  $\mu$  would be

$$\mu = \beta^{-1} \ln \left[ 1 - \exp(-2\pi\hbar^2 n_s \beta / gm) \right] + E_0 \quad (3.16')$$

Since  $g=3$  and  $m \sim 3m_o$  for the excitons in Cu<sub>2</sub>O, we can now fit the experimental data with  $n_s \sim 10^{12}$  cm<sup>-2</sup>. This value of  $n_s$  gives  $T_{c_\infty} \approx 3.3^\circ\text{K}$ . The value  $\epsilon_z \sim 10^{-6}$  V/m for the substrate fields may also be low due to a larger patch field.

It is obvious from these estimates that we must make a more careful examination of the shielding due to the exciton gas in Cu<sub>2</sub>O by including in our calculations band structure effects, exciton interactions, and the effects of electron-hole coupling. The condensation temperature for an interacting gas of excitons should also be studied. We will also explore the possibility that the condensed phase is superconducting. Finally, the excitonic gas in Cu<sub>2</sub>O was obtained by laser excitation in the experiments; we must study the possibility that a surface layer of excess electrons can also form the gas.

IV. Publications and Presentations.

The following papers are being prepared for publication:

1. "The Effects of Correlation on the Band Structure of TiO".
2. "Analysis of Energy Loss Spectra of Clean and Oxidized Titanium and Iron," with K. O. Legg.

The following paper is scheduled for presentation:

1. "Characteristic Energy Loss Spectra of Clean and Oxidized Titanium Surfaces," with K. O. Legg; March Meeting of the APS, Phoenix, Az. (1981). An abstract for this paper is attached to this section.

Abstract Submitted  
for the March Meeting of the  
American Physical Society

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Number 73

Suggested title of  
session in which paper  
should be placed:  
Energy Loss Spectroscopy

Characteristic Energy Loss Spectra of Clean and Oxidized Titanium Surfaces, M.W. Ribarsky and K.O. Legg, Georgia Institute of Technology.--We present recently taken energy loss spectra for clean and oxidized titanium and analyze the loss structures. The use of different primary electron energies and electron exit angles and comparisons with optical absorption data help identify surface and bulk plasmons and interband transitions. Our interpretation of the spectra, especially for the oxide, differs from earlier interpretations, and we discuss the implications of this for our view of characteristic losses in titanium oxide and for other processes occurring at the surface. We also analyze the plasmon structure in the light of various theoretical models.

V. Personnel

The following personnel have been partially compensated by funds provided in this grant for conducting the research during the period October 1, 1979 to September 30, 1980.

Dr. Martin W. Ribarsky - Research Scientist and Principal Investigator.

Mr. David Luedtke - Ph.D candidate.

VI. Interactions

We had the following interactions relative to this research during the period October 1, 1979 to September 30, 1980:

1. With Professor Joseph Callaway and his group at Louisiana State University about our modification and use of LCAO self-consistent band structure codes developed by his group.
2. With Peter Feibelman and Dwight Jennison at Sandia Laboratories about calculations on transition metal oxides to be used as a basis for calculating electronic excitation structure and plasmon structure.
3. With Dr. Brett Dunlap of N.R.L. about developing and using LCAO-X<sub>α</sub> cluster codes for the calculation of the electronic structure of surface oxides.

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